**Zn(ANA)2Cl2 complex as efficient catalyst for the synthesis of dihydropyrano[2,3-*c*]pyrazoles in aqueous medium *via* one-pot multicomponent reaction: a green approach**

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**1. Experimetal procedure and spectral data of [Zn(ANA)2Cl2] complex and Pyranopyrazoles**

***General procedure for the synthesis of [Zn(ANA)2Cl2 ] complex***

The freshly purified ligand (0.488 g, 4 mmol) was dissolved in EtOH (20 mL) and added ethanolic solution of ZnCl2.4H2O (0.273 g, 2 mmol) were stirred at reflux temperature after mixing the solution for about 3 h. At the end of the reaction the excess ethanol was removed in vacuum and filtered after cooling without further purification to obtain 75% yield. Yellow solid: mp 288-290 ˚C; IR (KBr, cm-1): 3412 (N-H), 1678 (C=O), 1564(C=N (py)). 1H NMR (400 MHz, DMSO): δ: 6.73-6.76 (m, 2H), 7.56 (s, 4H), 8.00 (d, *J* = 8.0 Hz, 2H), 8.24 (d, *J* = 8.0 Hz, 2H), 9.85 (s, 2H) ppm. 13C NMR (100 MHz, DMSO): δ: 112.69, 113.49, 145.08, 155.31, 158.68, 194.10 ppm. Anal. calcd (%) for Zn(C6H6N2O)2Cl2: Calcd: C, 37.85; H, 3.17; N, 14.72. Found: C, 37.80; H, 3.15; N 14.69.

***General procedure for the synthesis of the dihydropyrano[2,3-c]pyrazoles (4a-l)***

A mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol) and 3-Methyl-1-phenyl-2-pyrazoline-5-one (1 mmol) were stirred water at room temperature in the presence of 10 mol% of Zn(ANA)2Cl2 complex for appropriate time to produce dihydropyrano[2,3-c]pyrazoles. Reaction progress was monitored by TLC. After completion of the reaction the product was filtered. The residue was washed with ethyl acetate. The ethyl acetate was evaporated under vacuum and the obtained solid was purified by recrystalization process in ethyl acetate.

1. **Spectral data of the compound 4a-l**
   1. **6-amino-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4a):** Colour: White solid; M. P.: 168-170 ˚C; Anal. Calcd. For C20H16N4O: C, 73.15; H, 4.91; N, 17.06; found: C, 73.37; H, 4.98; N, 17.29. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.79 (s, 3H), 4.89 (s, 1H), 7.22-7.36 (m, 8H), 7.5 (d, 2H, *J* = 7.6 Hz), 7.8 (d, 2H, *J* = 7.6 Hz). 13C NMR (100 MHz, DMSO) *δ*: 159.90, 145.75, 144.36, 144.08, 138.02, 129.80, 129.00, 128.25, 127.52, 126.63, 120.43, 99.11, 58.68, 37.23, 13.03.
   2. **6-amino-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4b):** Colour:White solid; M. P.: 187-189 ˚C; Anal. Calcd. For C20H15N5O3: C, 64.34; H, 4.05; N, 18.76; found: C, 64.59; H, 4.11; N, 18.49. 1H NMR (DMSO-d6, 400 MHz) *δ:* 1.81 (s, 3H), 4.99 (s, 1H), 7.34 (t, 1H, *J* = 7.2 Hz), 7.42 (s, 2H), 7.51 (t, 2H, *J* = 7.6 Hz), 7.69 (t, 1H, *J* = 8.4 Hz), 7.79- 7.82 (m,3H), 8.17 (bs, 2H). 13C NMR (100 MHz, DMSO) *δ*: 160.23, 148.42, 146.45, 145.63, 144.50, 137.91, 135.25, 130.76, 129.80, 129.39, 126.77, 122.76, 122.73, 120.58, 120.28, 98.13, 57.53, 36.67, 13.08.
   3. **6-amino-3-methyl-4-(2-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4c):** Colour**:** White solid; M. P.: 156-158 ˚C; Anal. Calcd. For C20H15N5O3: C, 64.34; H, 4.05; N, 18.76; found: C, 64.02; H, 4.15; N, 18.98. 1H NMR (DMSO-d6, 400 MHz) *δ:* 1.76 (s, 3H), 5.21 (s, 1H), 7.32-7.39 (m, 3H), 7.49-7.56 ( m, 4H), 7.7 (t, 1H, *J* = 7.6 Hz), 7.8 (d, 2H, *J* = 8.00 Hz), 7.91(d, 1H, *J* =8.00 Hz). 13C NMR (100 MHz, DMSO) *δ*: 160.26, 149.75, 147.25, 145.36, 144.83, 138.18, 137.89, 137.17, 133.89, 132.12, 129.82, 129.11, 126.82, 124.19, 120.59, 119.96, 97.78, 57.28, 32.38, 12.75.
   4. **6-amino-4-(3,4-dimethylphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4d):** Colour:White solid; M. P.: 150-151 ˚C; Anal. Calcd. For C22H20N4O: C, 74.14; H, 5.66; N, 15.72; found: C, 74.39; H, 5.75; N, 15.51. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.82 (s, 3H), 3.72 (s, 3H), 3.74 (s,3H), 4.64 (s, 1H), 6.75-6.93 (m, 3H), 7.17 (s, 2H) 7.32 (t, 1H, *J* = 7.2 Hz), 7.49 (t, 2H, *J* = 7.6 Hz), 7.79 (d, 2H, *J* = 8.00 Hz).13C NMR (100 MHz, DMSO) *δ*: 159.80, 149.09, 148.28, 145.86, 144.27, 138.07, 136.52, 129.79, 126.57, 120.55, 120.35, 112.26, 112.03, 99.18, 58.90, 56.04, 55.93, 36.65, 13.15.
   5. **6-amino-4-(4-cyanophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4e):** Colour:White solid; M. P. 198-200 ˚C; Anal. Calcd. For C21H15N5O: C, 71.38; H, 4.28; N, 19.82; found: C, 71.62; H, 4.34; N, 19.69. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.79 (s, 3H), 4.85 (s, 1H), 7.34 (t, 1H, *J* = 7.2 Hz), 7.39 (s, 2H), 7.49-7.52 (m, 4H), 7.80-7.86(m, 4H).13C NMR (100 MHz, DMSO) *δ*: 160.17, 149.66, 145.59, 144.50, 137.92, 133.11, 129.79, 129.43, 126.75, 120.57, 120.25, 119.24, 110.43, 98.11, 57.50, 37.13, 13.01.
   6. **6-amino-4-(4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4f):** Colour**:** White solid; M. P. 205-207 ˚C; Anal. Calcd. For C20H16N4O2: C, 69.76; H, 4.68; N, 16.27; found: C, 69.91; H, 4.75; N, 16.11. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.81 (s, 3H), 4.57 (s, 1H), 6.76 (s, 2H), 7.06 (s, 2H), 7.17 (s, 2H), 7.31(s, 1H), 7.49 (s,2H), 7.80 (s,2H), 9.39 (s,1H).13C NMR (100 MHz, DMSO) *δ*: 159.67, 156.77, 145.84, 144.24, 138.07, 134.41, 129.78, 129.26, 126.52, 120.62, 120.33, 115.70, 99.50, 59.27, 36.50, 19.03.
   7. **6-amino-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4g):** Colour:pale yellow solid; M. P.: 176-178 ˚C; Anal. Calcd. For C20H15ClN4O: C, 66.21; H, 4.17; Cl, 9.77; N, 15.44; found: C, 66.43; H, 4.10; Cl, 9.58; N, 15.19. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.82 (s, 3H), 4.73 (s, 1H), 7.27-7.34 (m, 5H), 7.42 (d, 2H, *J* = 8.00 Hz), 7.5 (t, 2H, *J* = 7.2 Hz), 7.8 (d, 2H, *J* = 7.6 Hz). 13C NMR (100 MHz, DMSO) δ: 159.95, 145.67, 144.40, 143.14, 137.97, 132.06, 130.18, 129.80, 129.01, 126.69, 120.50, 120.34, 98.66, 58.24, 36.56, 13.04.
   8. **6-amino-4-(2,4-dichlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4h):** Colour**:** White solid; M. P.: 183-185 ˚C; Anal. Calcd. For C20H14Cl2N4O: C, 60.47; H, 3.55; Cl, 17.85; N, 14.10; found: C, 60.69; H, 3.49; Cl, 17.66; N, 14.39. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.78 (s, 3H), 5.16 (s, 1H), 7.32 (d, 1H), 7.36 (s, 2H,), 7.39-7.63 (m, 5H,), 7.78-7.80 (d, 2H). 13C NMR (100 MHz, DMSO) *δ*: 160.42, 145.30, 144.75, 139.74, 137.90, 133.55, 133.02, 132.97, 30.54, 129.82, 129.43, 128.59, 126.78, 120.53, 120.01, 97.76, 56.62, 34.02, 12.82.
   9. **6-amino-4-(4-bromophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4i):** Colour:White solid; M. P.: 182-184 ˚C; Anal. Calcd. For C22H21N5O: C, 71.14; H, 5.70; N, 18.85; found: C, 71.35; H, 5.75; N, 18.63. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.8 (s, 3H), 4.72 (s, 1H), 7.23-7.34 (m, 5H), 7.48-7.6 ( m, 4H), 7.79 (d, 2H, *J* = 8.00 Hz). 13C NMR (100 MHz, DMSO) δ: 159.95, 145.67, 144.40, 143.56, 137.96, 131.93, 130.54, 129.80, 126.69, 120.60, 120.49, 120.34, 98.59, 58.16, 36.62, 13.05.
   10. **6-amino-4-(4-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4j):** Colour:White solid; M. P.: 172-174 ˚C; Anal. Calcd. For C21H18N4O2: C, 70.38; H, 5.06; N, 15.63; found: C, 69.69; H, 5.85; N, 6.19. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.79 (s, 3H), 3.75 (s, 3H), 4.63 (s,1H), 6.91 (d, 1H, *J* = 8.4 HZ), 7.16-7.18 (m, 3H), 7.31 (t, 1H, *J* = 7.2 Hz), 7.38 (t, 1H, *J* = 7.6 Hz), 7.49 (t, 2H, *J* = 7.6 Hz), 7.79 (d, 3H, *J* = 8.4 Hz).
   11. **6-amino-4-(3-ethoxy-4-hydroxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4k):** Colour:White solid; M. P.: 167-169 ˚C; Anal. Calcd. For C22H20N4O3: C, 68.03; H, 5.19; N, 14.42; found: C, 69.69; H, 5.85; N, 6.19. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.30 (t, 3H, *J* = 6.8 Hz), 1.82 (s, 3H), 3.96-4.01 (m, 2H), 4.56 (s, 1H), 6.61-7.13 (m, 5H), 7.31 (t, 1H, *J* = 7.2 Hz), 7.49 (t, 2H, *J* = 7.6 Hz) 7.79 (d, 2H, *J* = 8.4 Hz), 8.83 (s, 1H). 13C NMR (100 MHz, DMSO) δ: 159.69, 146.91, 146.30, 145.87, 144.23, 138.09, 134.97, 129.79, 126.53, 120.66, 120.57, 120.31, 116.09, 113.96, 99.36, 64.44, 59.15, 36.79, 15.18, 13.13.
   12. **6-amino-3-methyl-4-(4-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (4l):** Colour**:** white solid; M. P.: 191-193 ˚C; . Anal. Calcd. For C20H15N5O3: C, 64.34; H, 4.05; N, 18.76; found: C, 64.61; H, 3.97; N, 18.98. 1H NMR (DMSO-d6, 400 MHz) *δ*: 1.82 (s, 3H), 4.94 (s, 1H), 7.44-7.6 (m, 7H), 7.83 (bs, 2H), 8.25 (bs, 2H). 13C NMR (100 MHz, DMSO) *δ*: 160.20, 151.66, 147.08, 145.62, 144.48, 137.91, 129.79, 129.68, 126.76, 124.36, 120.54, 120.23, 98.05, 57.38, 36.90, 13.03.

**2. Characterization spectra (1H-NMR, 13C-NMR) of the synthesized compounds (4a-l).**

Fig. 1: 1HNMR spectrum of the compound **4a**.

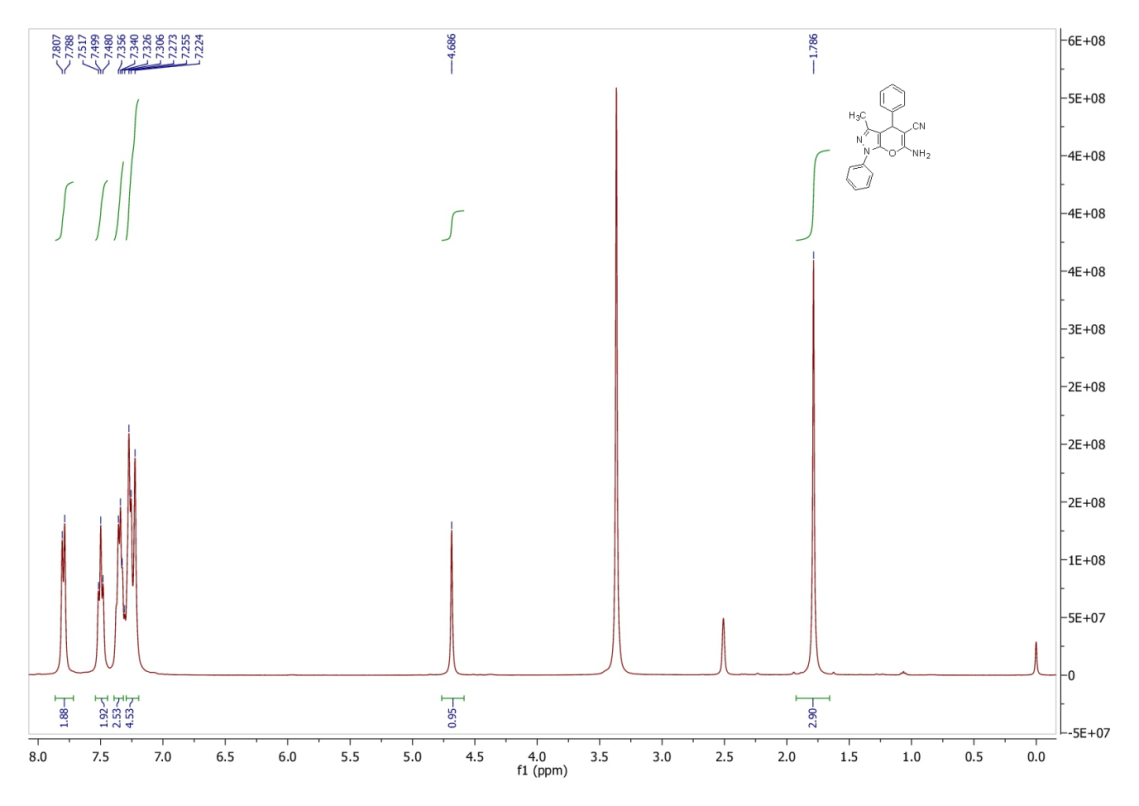


Fig. 2: 13CNMR spectrum of the compound 4**a**.

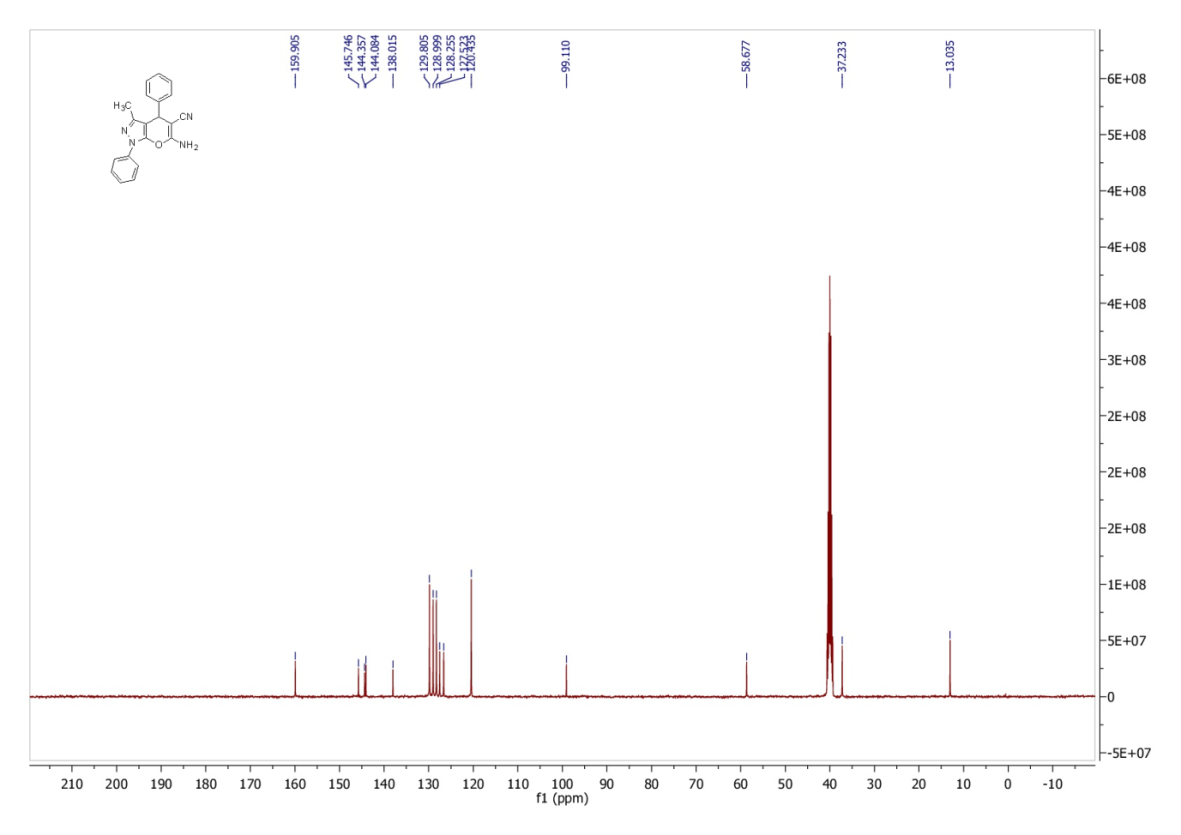
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Fig. 3: 1HNMR spectrum of the compound **4b**.

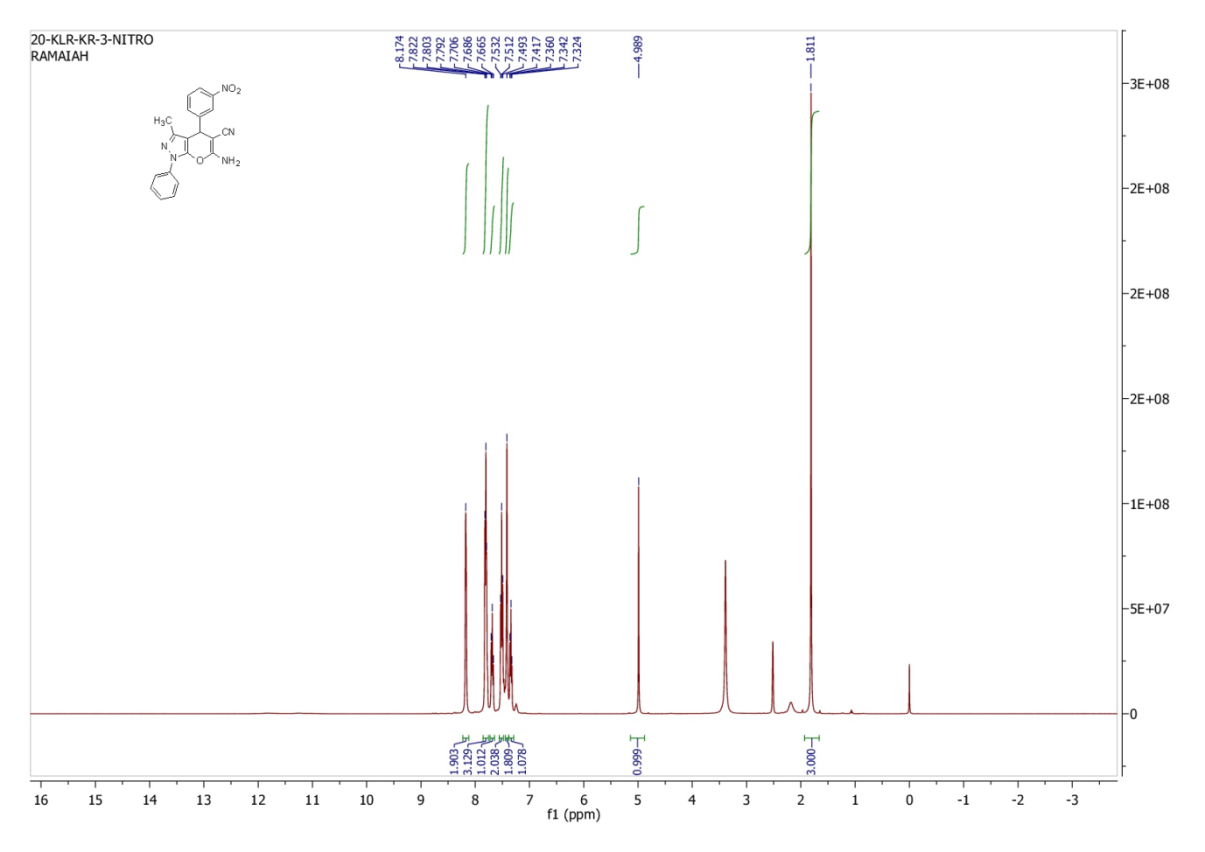


Fig. 4: 13CNMR spectrum of the compound **4b**.

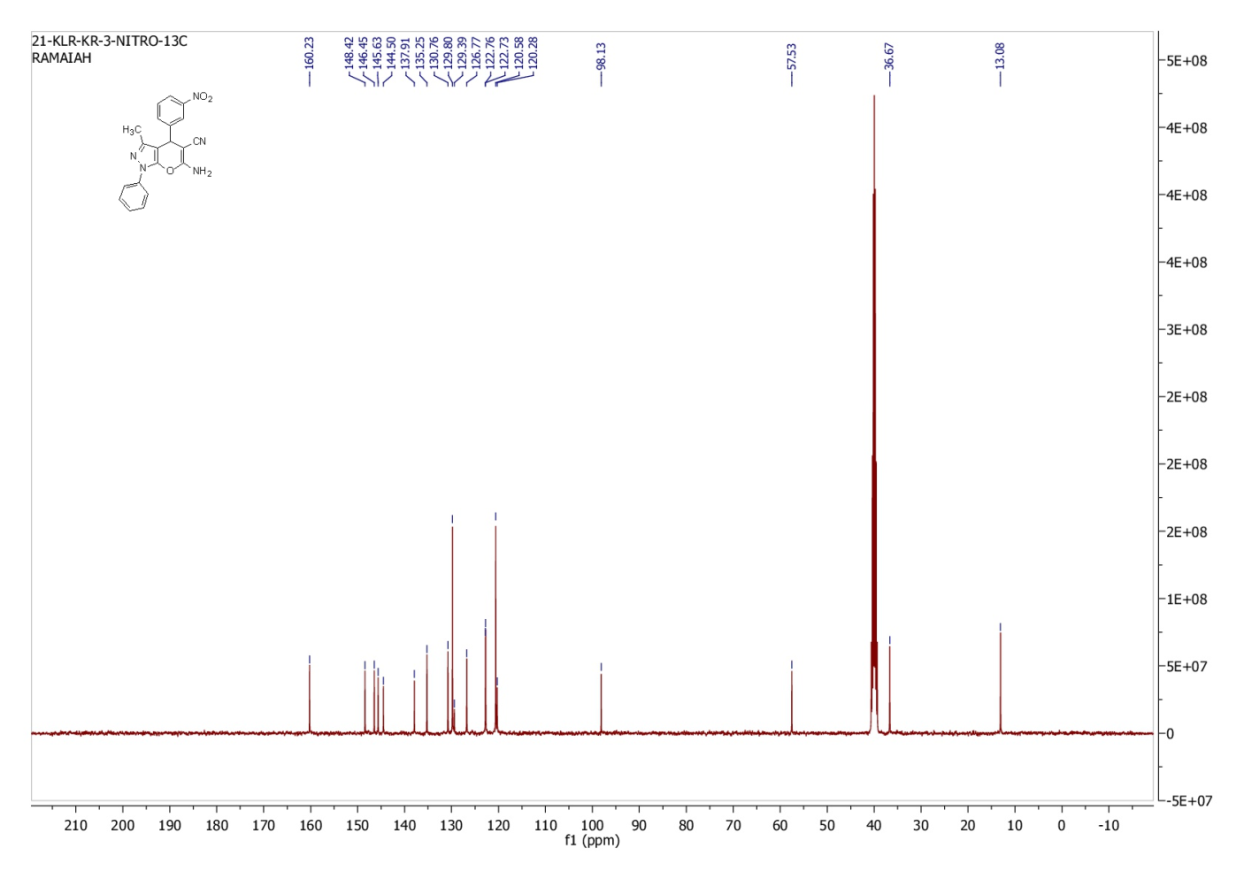


Fig. 5: 1HNMR spectrum of the compound **4c**.

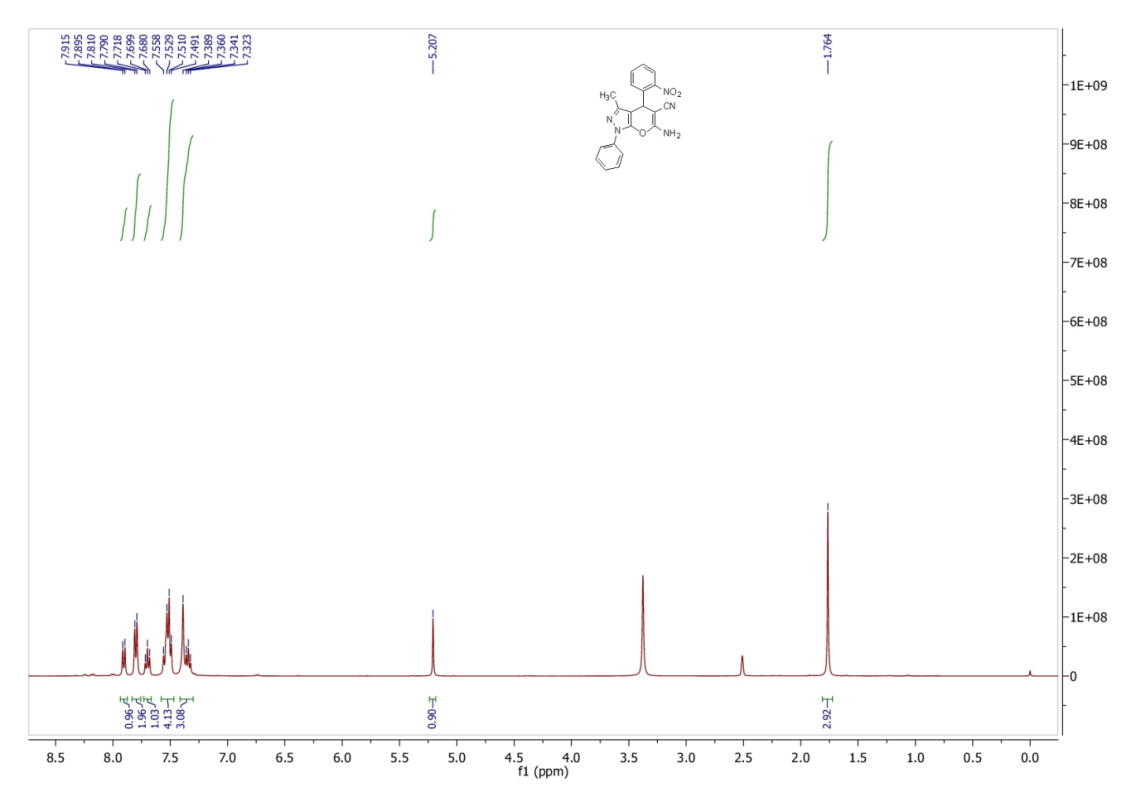


Fig. 6: 13CNMR spectrum of the compound **4c**.

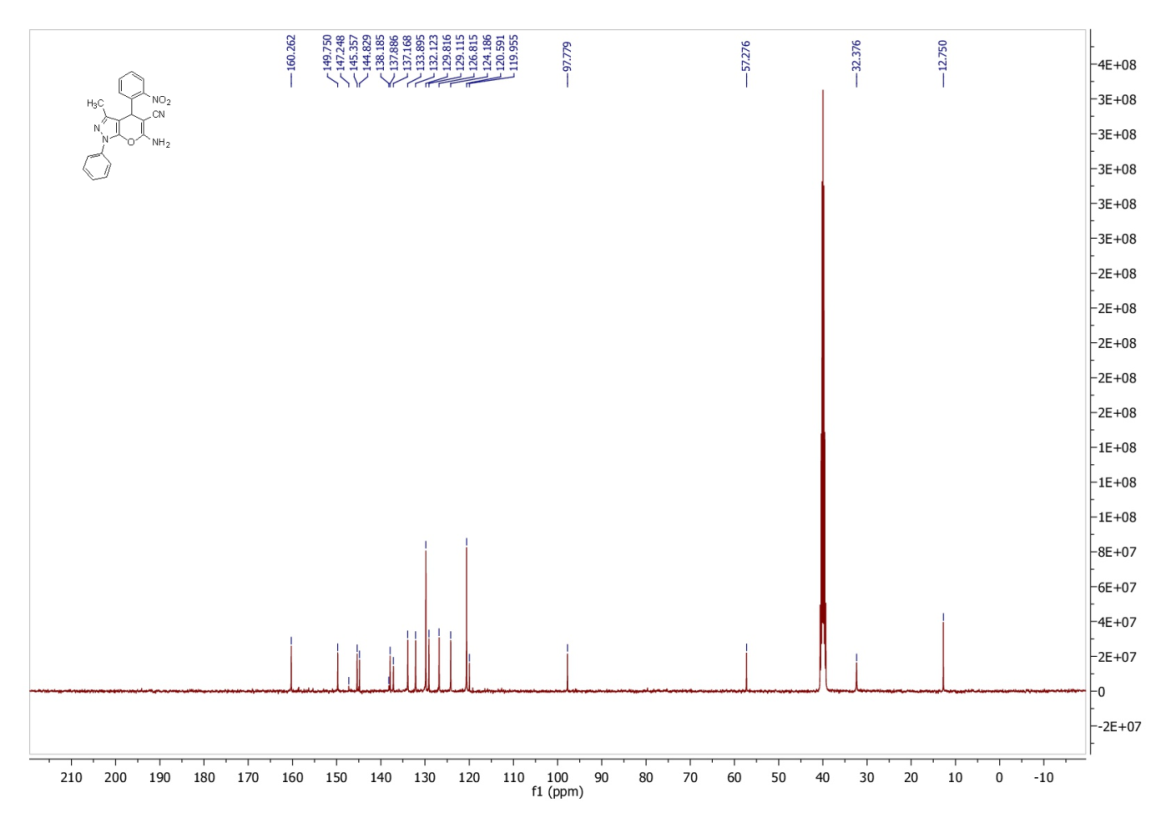


Fig. 7: 1HNMR spectrum of the compound **4d**.

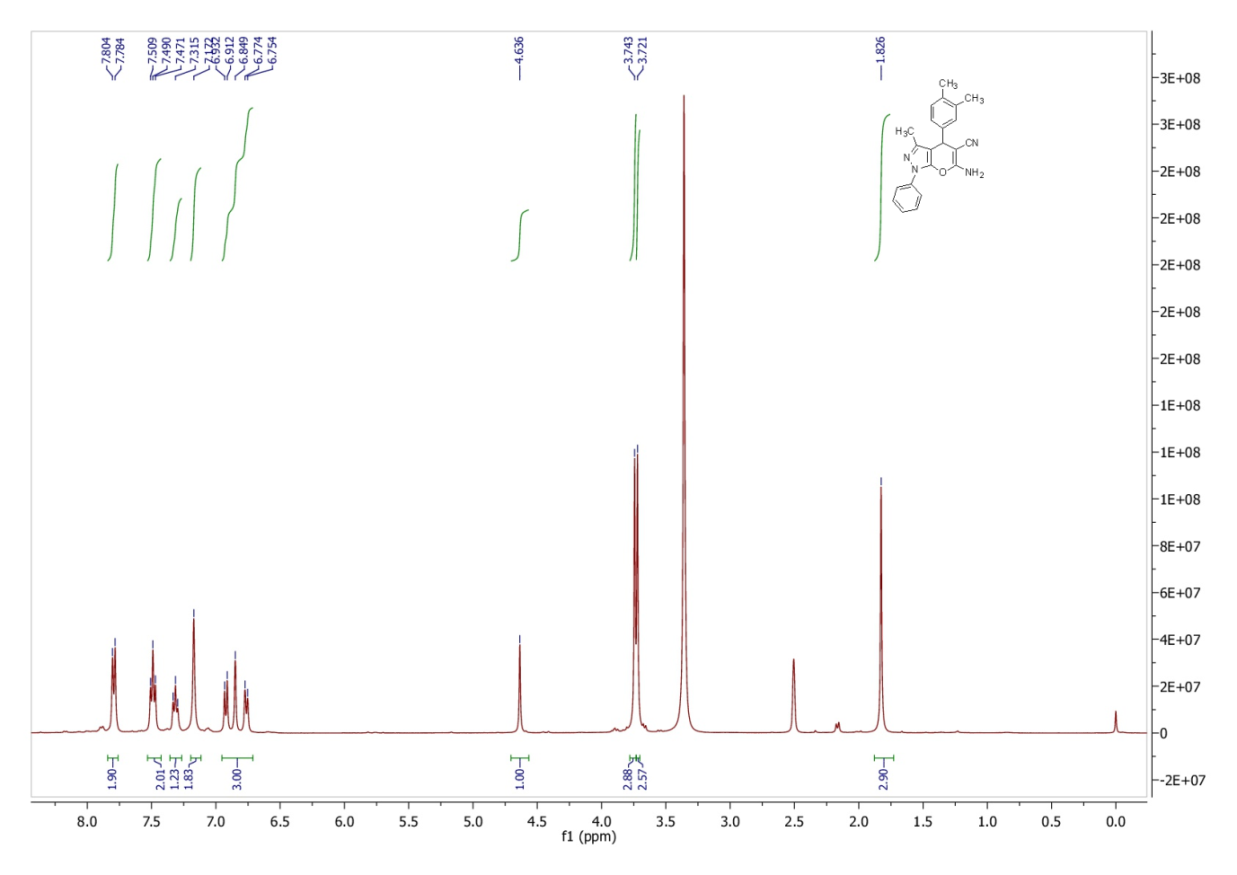


Fig. 8: 13CNMR spectrum of the compound **4d**.

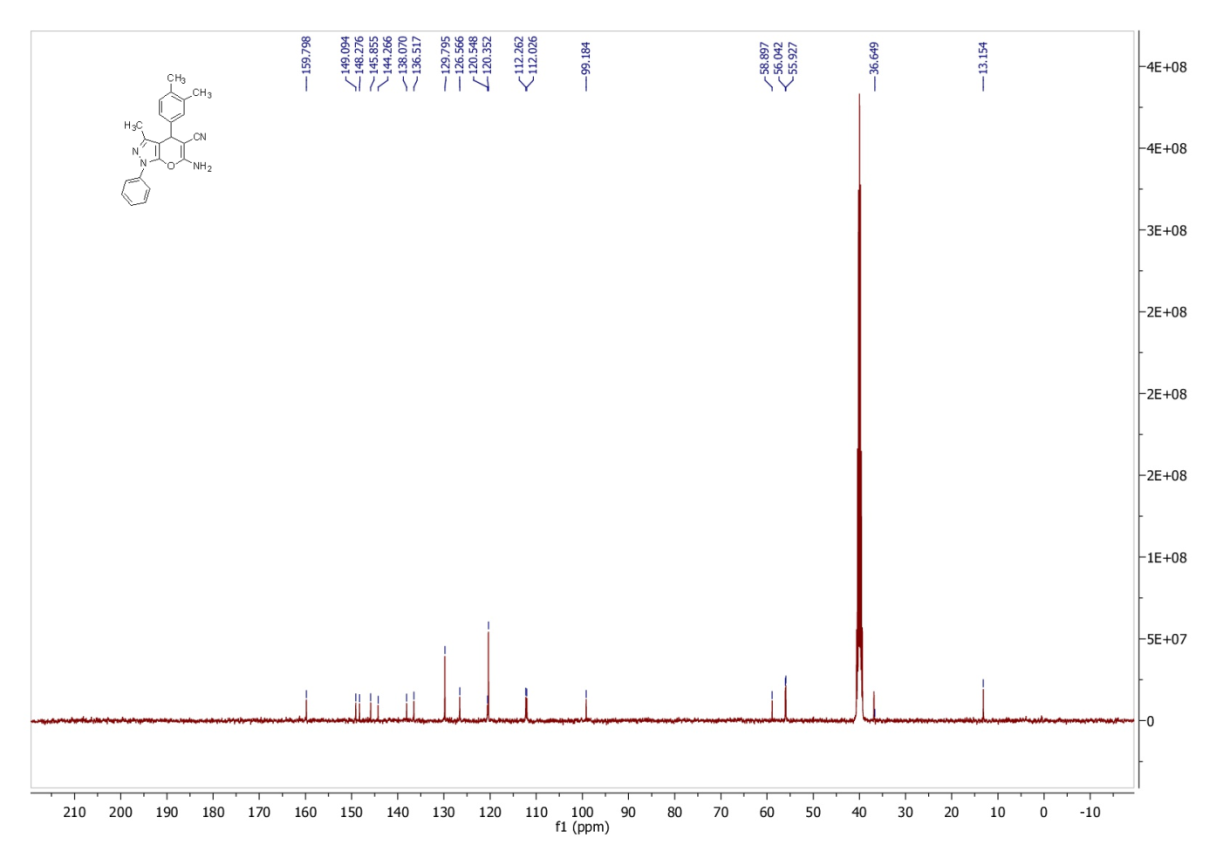


Fig. 9: 1HNMR spectrum of the compound **4e**.

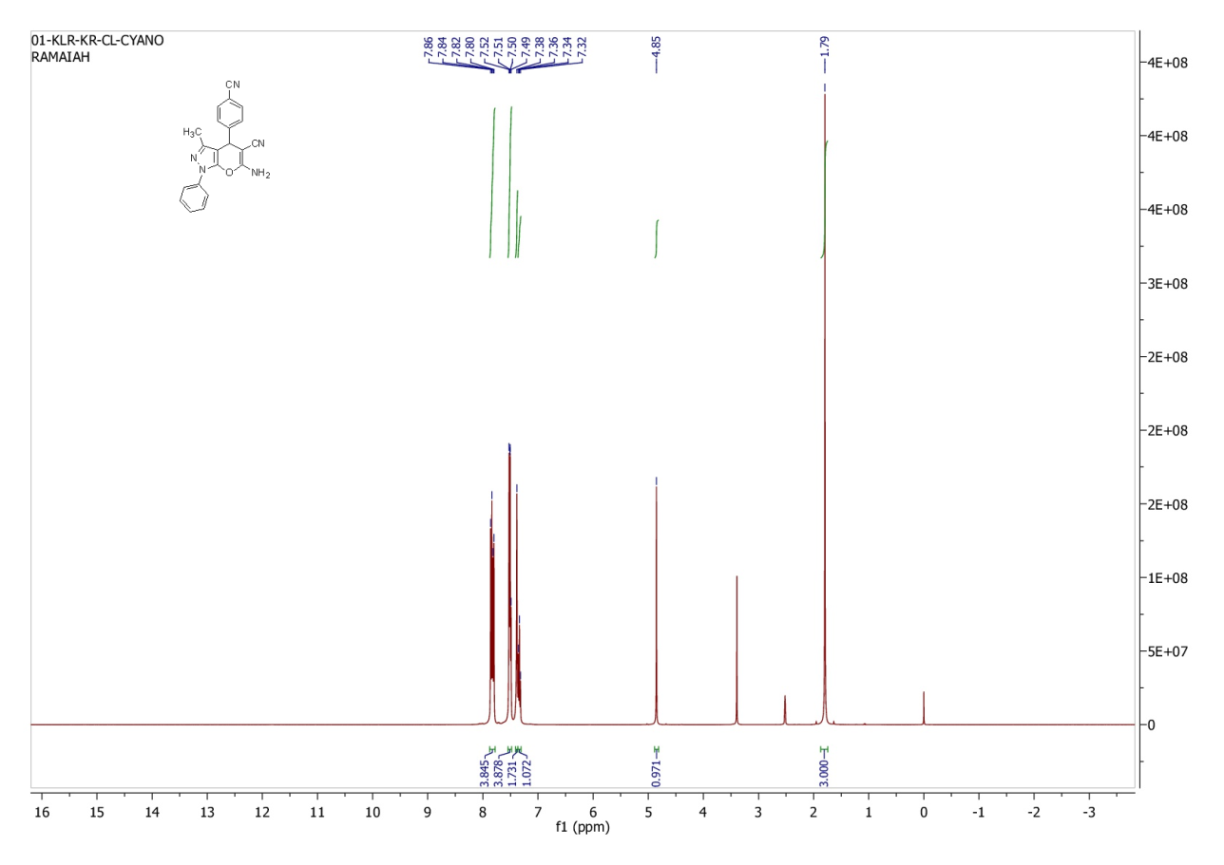


Fig. 10: 13CNMR spectrum of the compound **4e**.

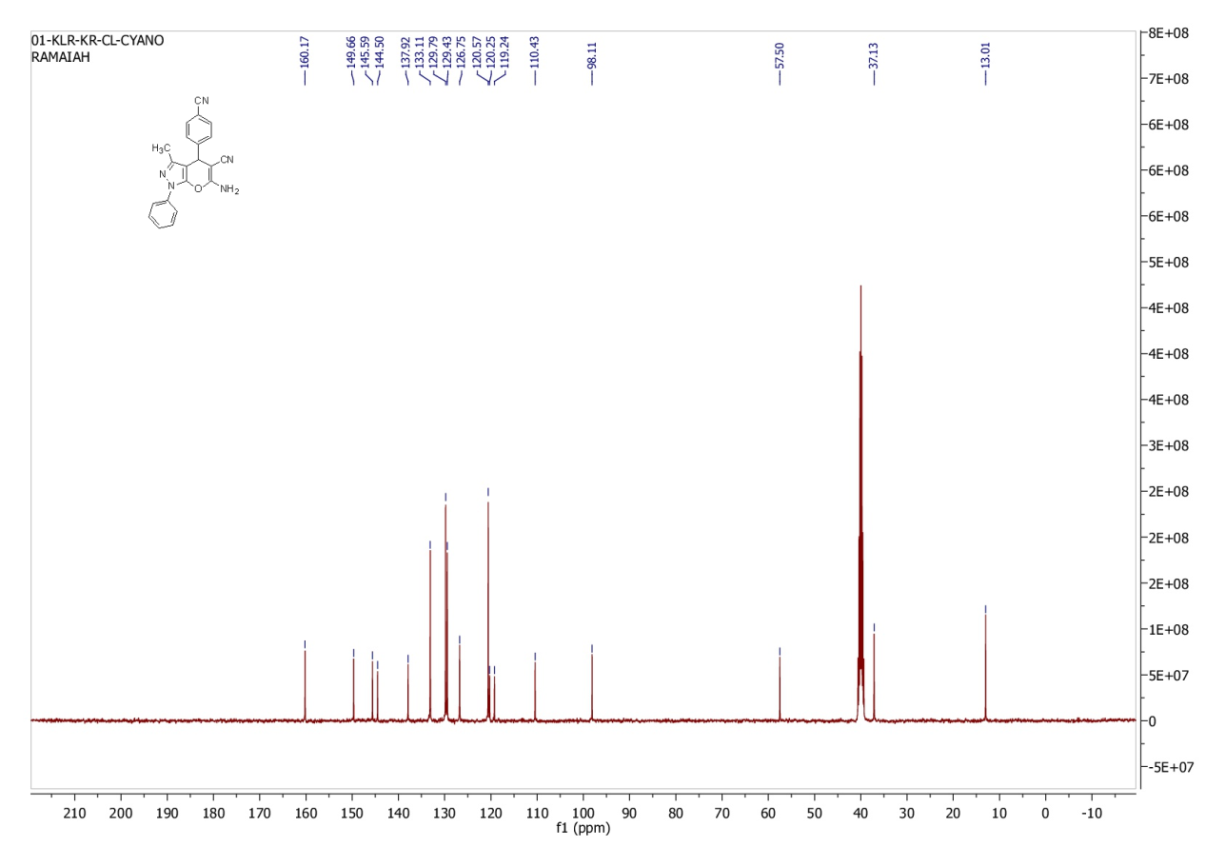


Fig. 11: 1HNMR spectrum of the compound **4f**.

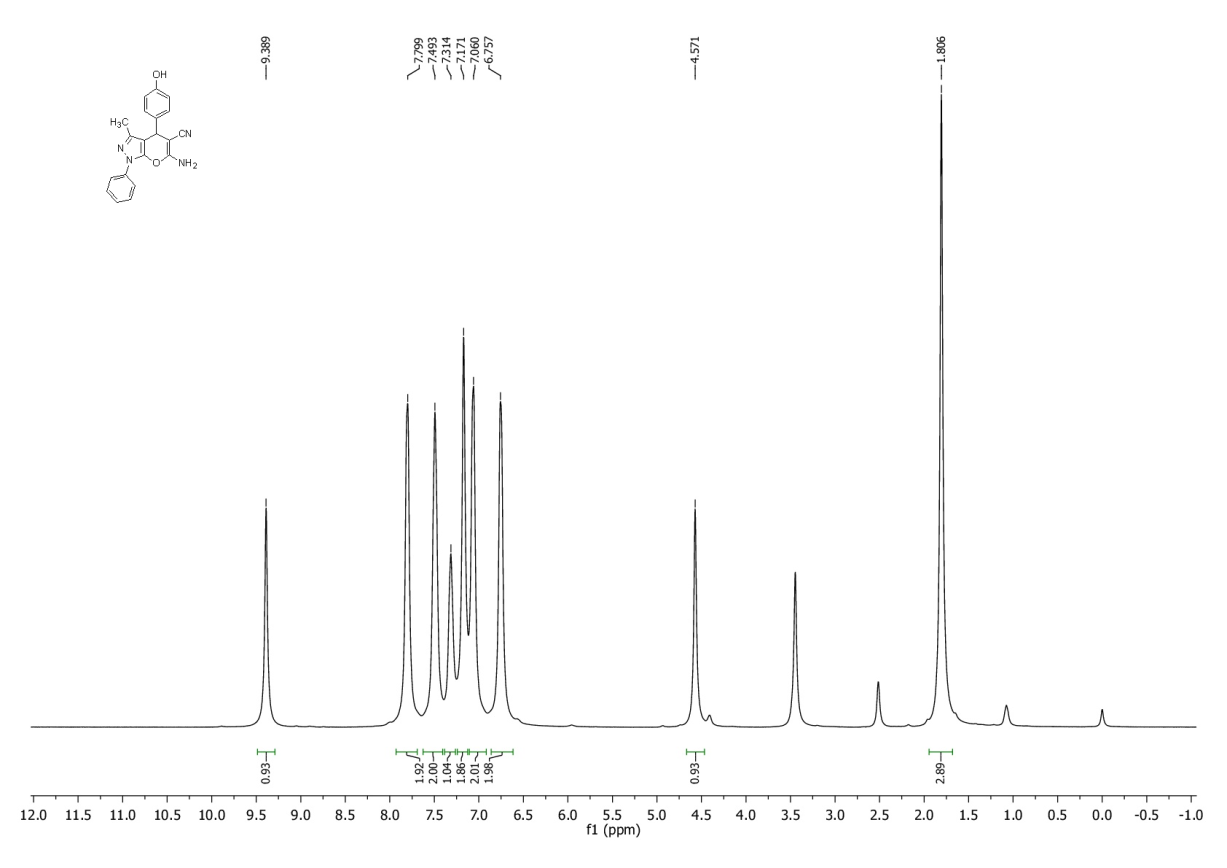


Fig. 12: 13CNMR spectrum of the compound **4f**.

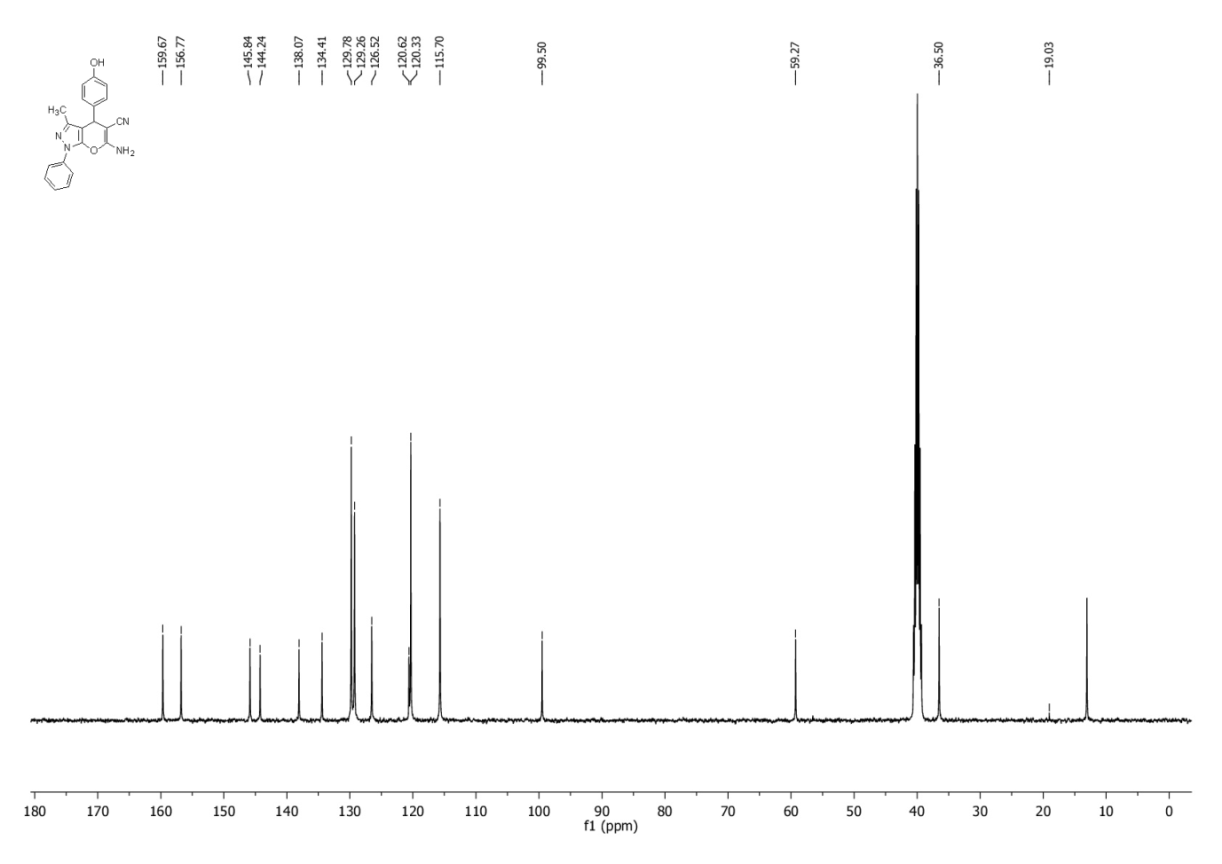


Fig. 13: 1HNMR spectrum of the compound **4g**.

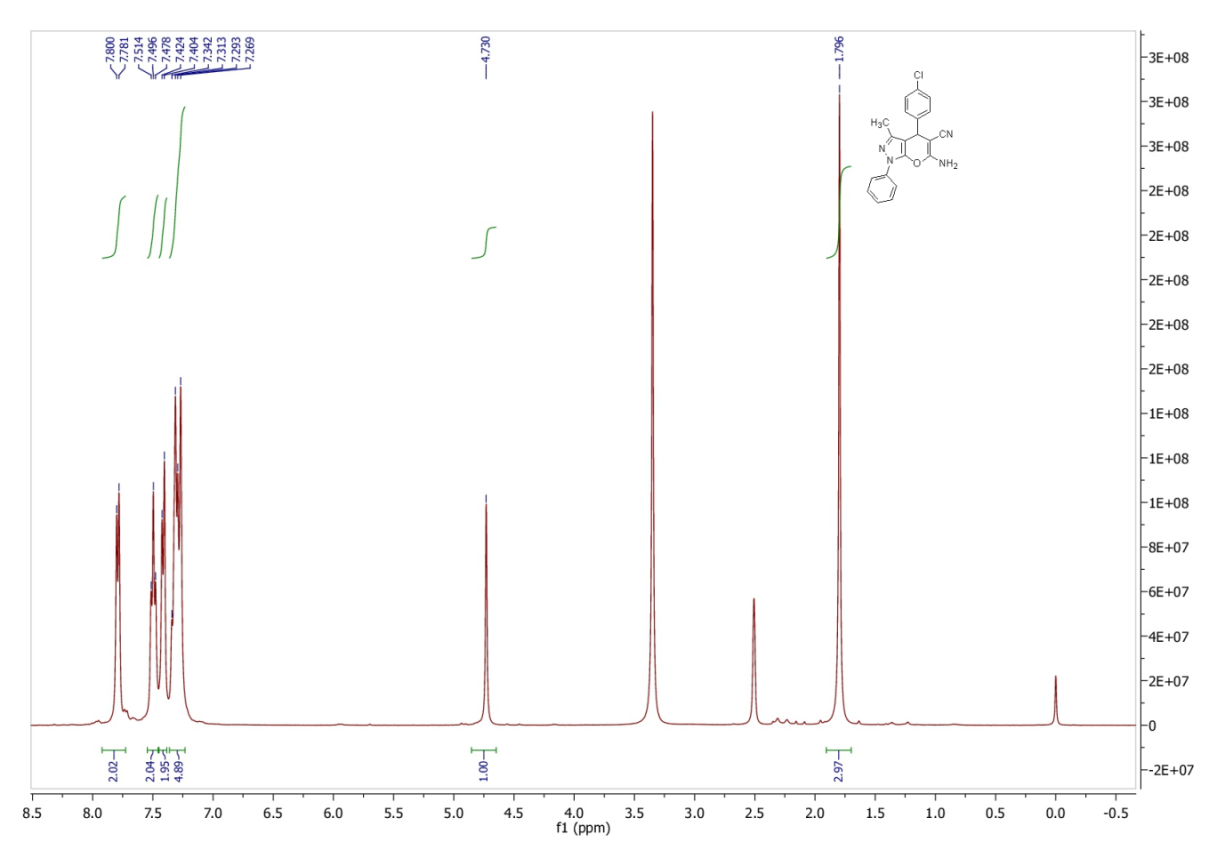


Fig. 14: 13CNMR spectrum of the compound **4g**.

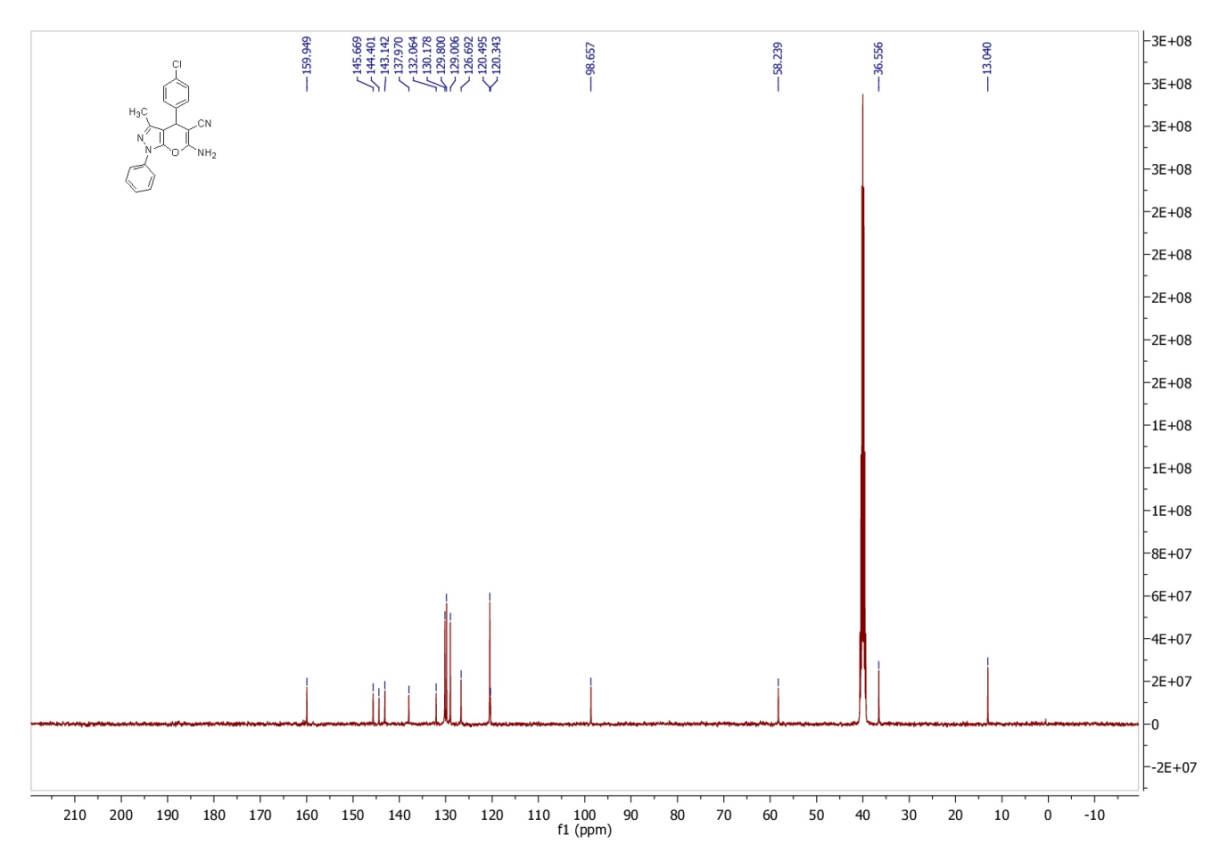


Fig. 15: 1HNMR spectrum of the compound **4h**.

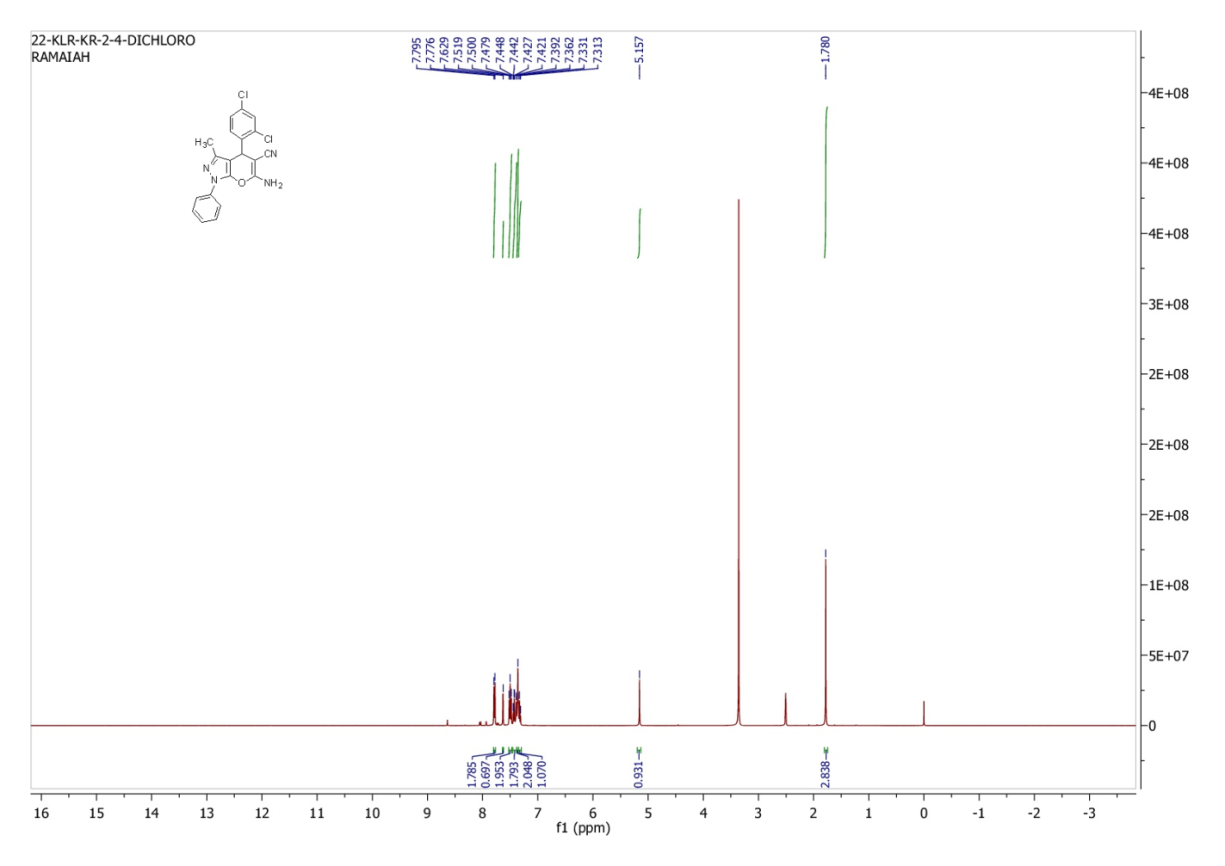


Fig. 16: 13CNMR spectrum of the compound **4h**.

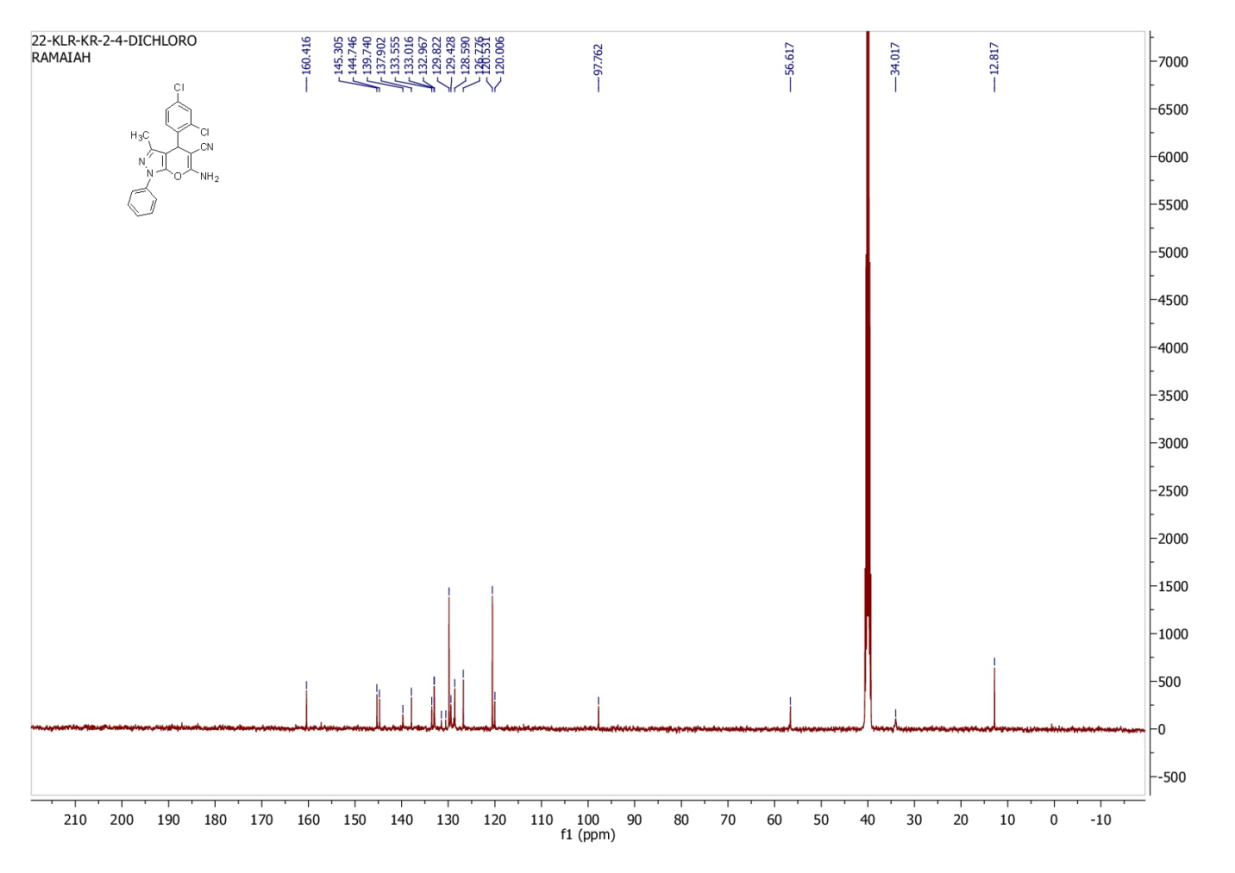


Fig. 17: 1HNMR spectrum of the compound **4i**.

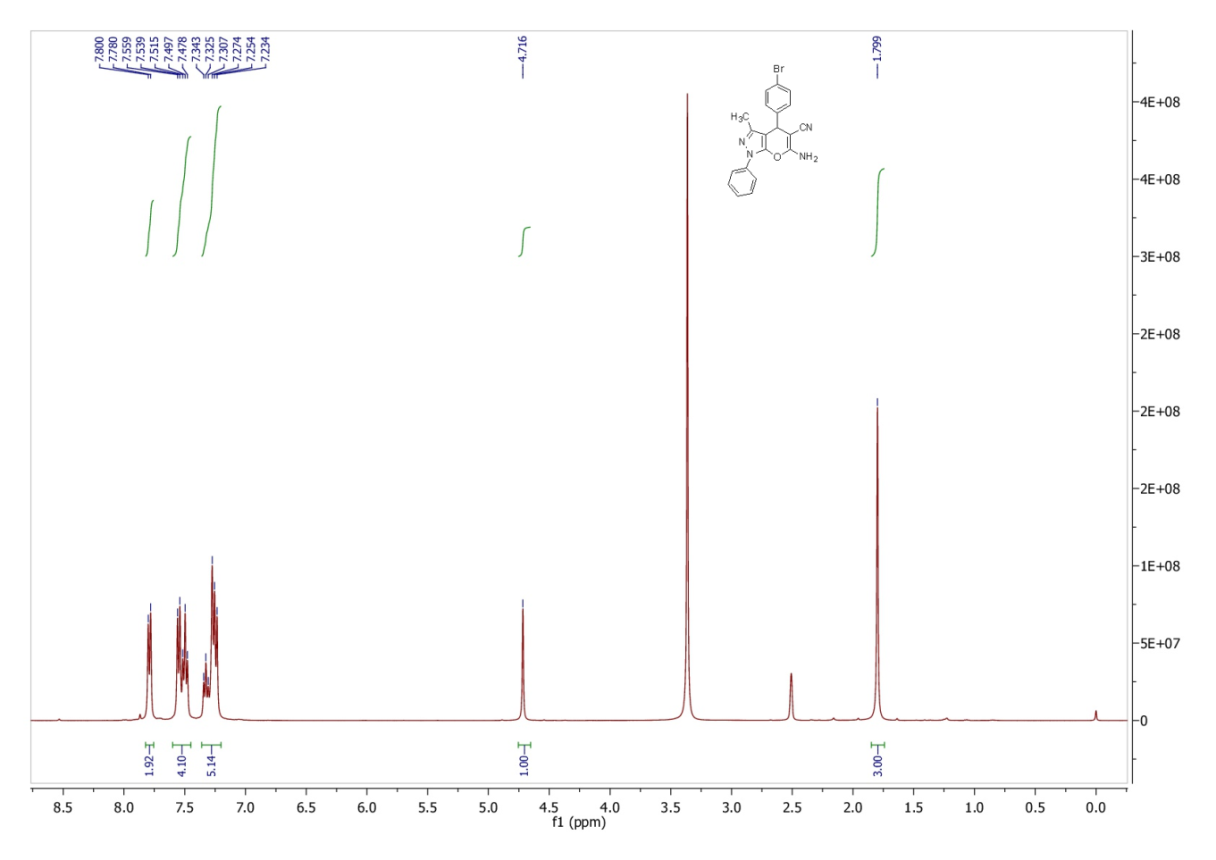


Fig. 18: 13CNMR spectrum of the compound **4i**.

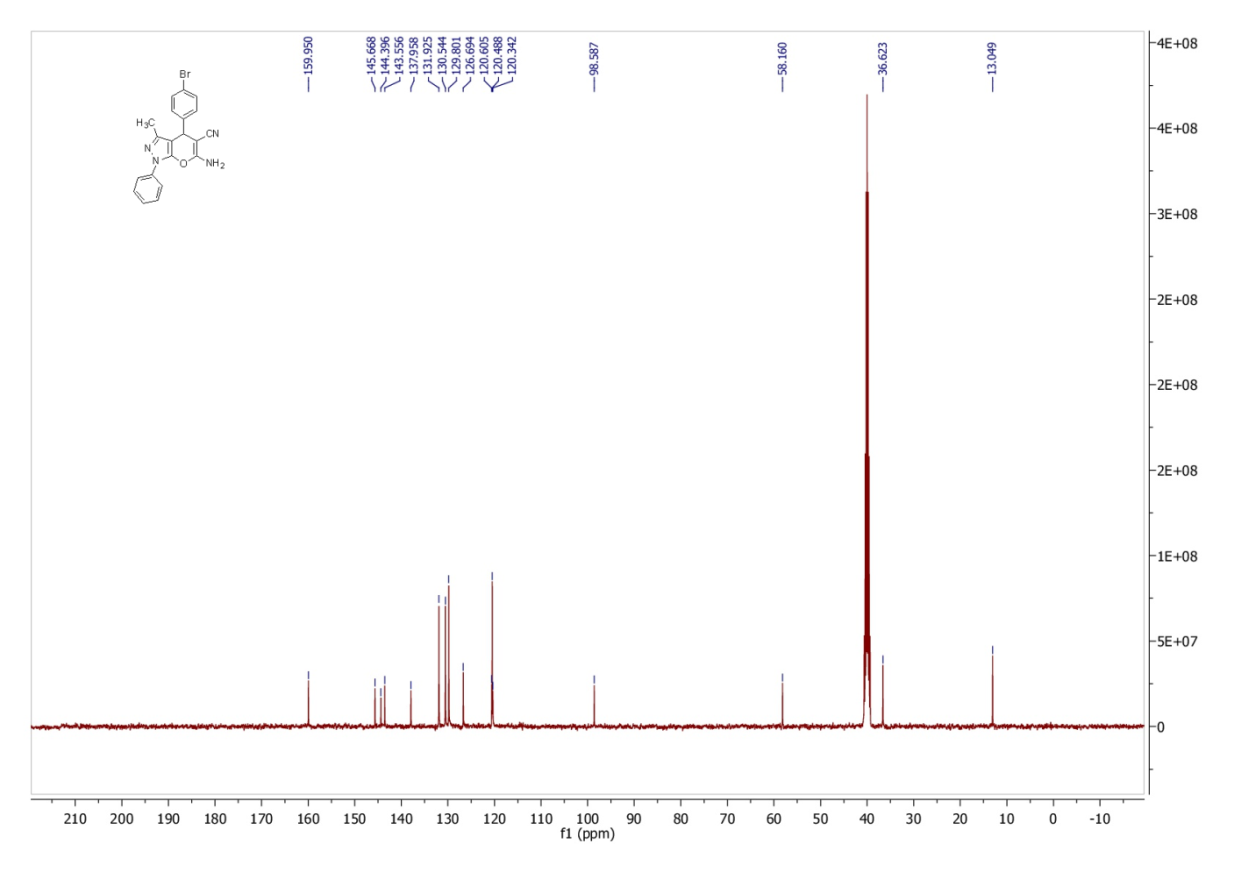


Fig. 19: 1HNMR spectrum of the compound **4j**.

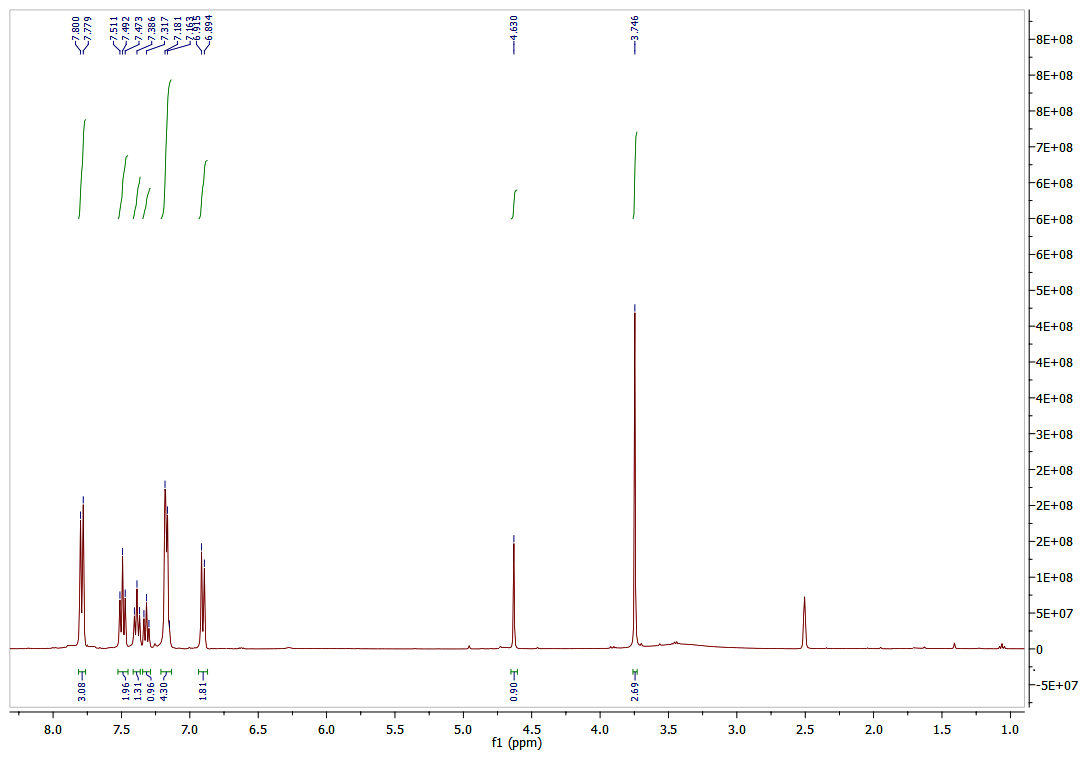


Fig. 20: 1HNMR spectrum of the compound **4k**.

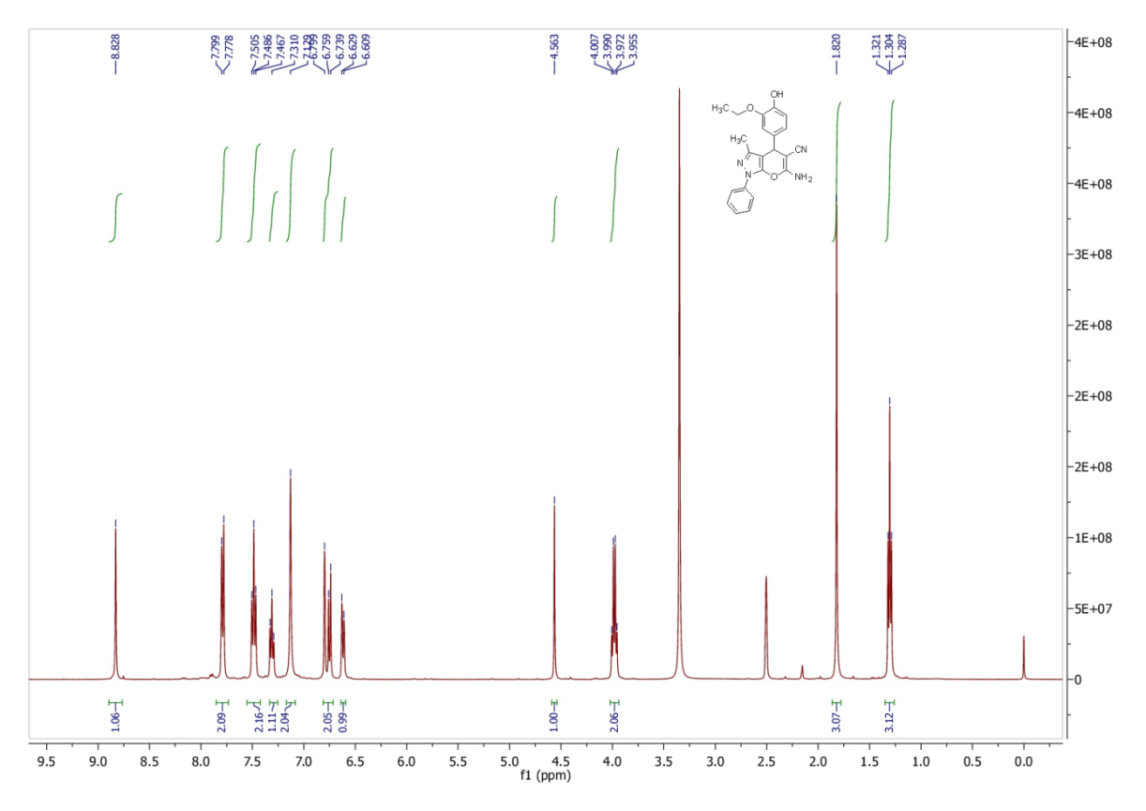


Fig. 21: 13CNMR spectrum of the compound **4k**.

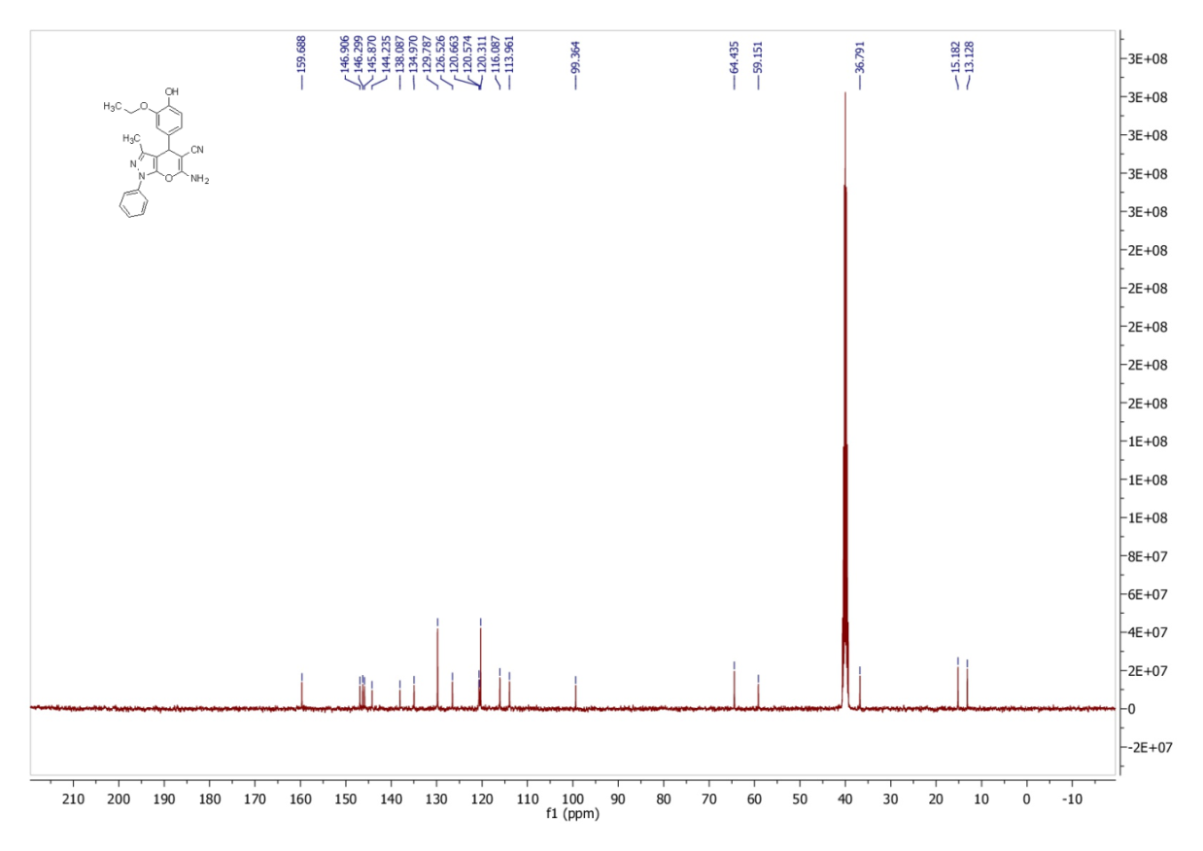


Fig. 22: 1HNMR spectrum of the compound **4l**.

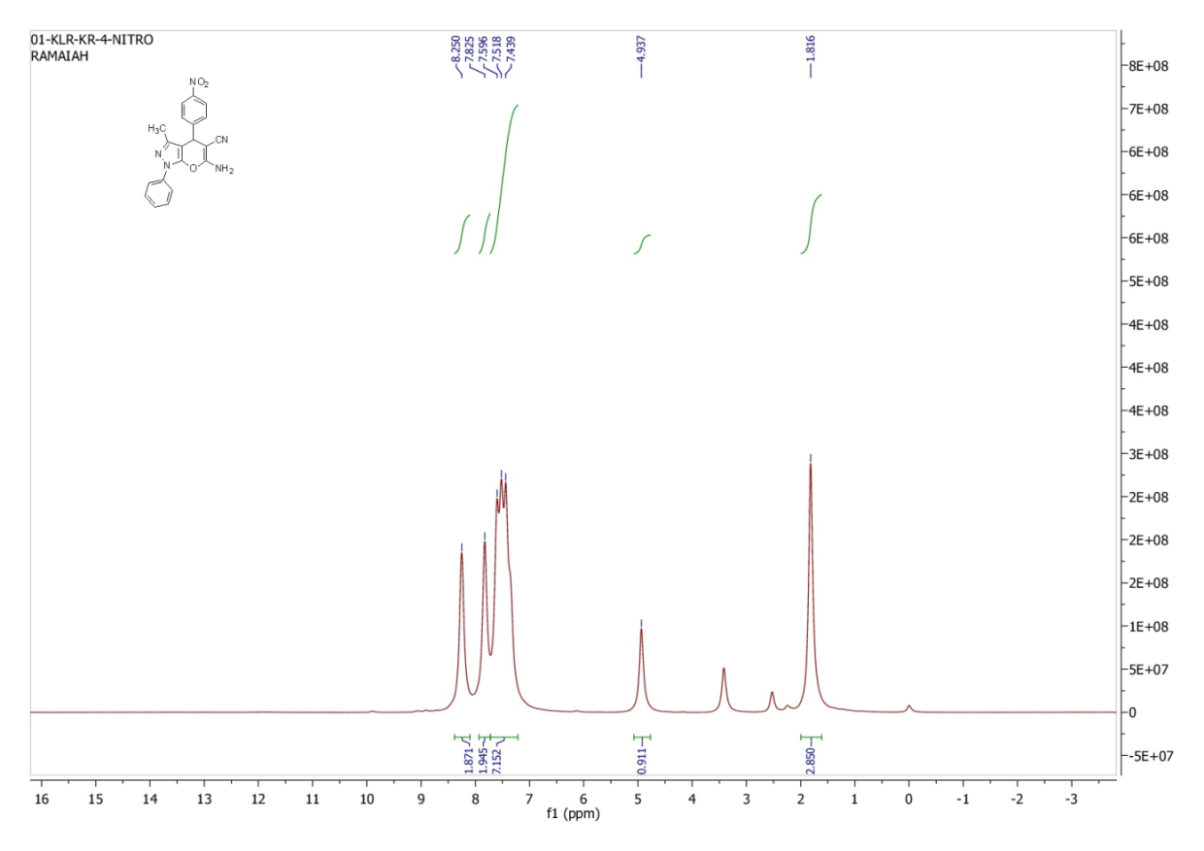
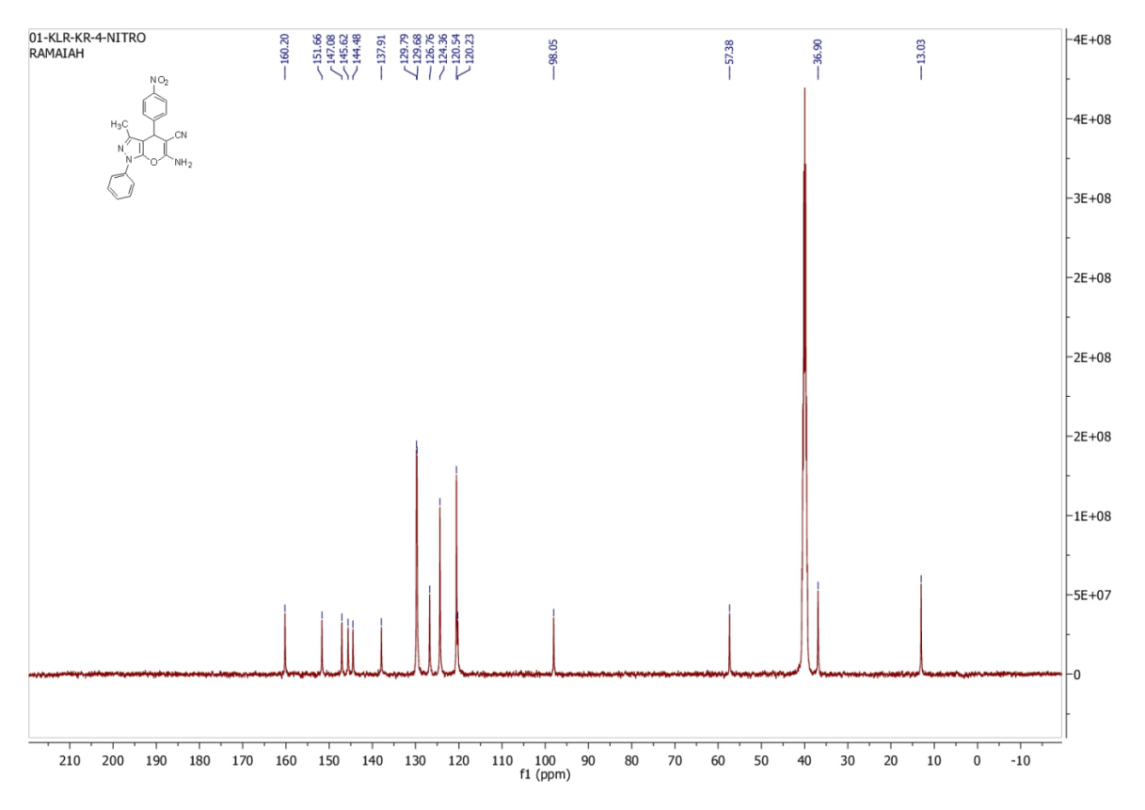


Fig. 23: 13CNMR spectrum of the compound **4l**.



**Fig.** **S1**.

**The schemetic representaion of Zn catalyst from SXRD method**

